

## Scientific Note

### AN ALTERNATIVE METHOD TO MEASURE AVAILABLE SULPHUR BY ION CHROMATOGRAPHY IN VOLCANIC SOILS

## Nota Científica

### UN MÉTODO ALTERNATIVO PARA MEDIR EL AZUFRE DISPONIBLE POR CROMATOGRAFÍA IÓNICA EN SUELOS VOLCÁNICOS

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## RESUMEN

El azufre (S) es un nutriente esencial para los cultivos, y recientemente se han registrado deficiencias en algunos suelos. El índice de fertilidad de S se basa en la disponibilidad de sulfato medido a través de turbidimetría (TB), que es un método fácil y rápido de aplicar. Este método es muy variable e impreciso, especialmente en Andisoles, por lo que la evaluación de la fertilidad de S en estos suelos no es confiable. El objetivo de este estudio fue evaluar la aplicabilidad del método de cromatografía iónica (IC) para medir con más exactitud y precisión el S disponible en suelos volcánicos de Chile. Se evaluó el contenido de sulfato disponible en dos sitios con suelos y climas contrastantes, a través de TB e IC. Se probó la exactitud y precisión del método IC calculando la curva de calibración y comparando la concentración de sulfato en extractos de suelo ( $n = 10$ ) con la adición de concentraciones conocidas en los mismos extractos. El S disponible en el Andisol no obtuvo el mismo valor de acuerdo a la metodología empleada ( $P \leq 0,05$ ), y no se observaron diferencias en el Inceptisol ( $P > 0,05$ ). El método IC mostró linealidad ( $R^2 = 0,9998$ ) y precisión, sin diferencias significativas entre el valor de sulfato medido y el modelado ( $P \geq 0,05$ ). Un amplio rango de S disponible fue medido en otros suelos usando IC ( $7-37 \text{ mg SO}_4^{-2} \text{ kg suelo}^{-1}$ ), demostrando los diferentes suministros de S en Andisoles y la importancia de aplicar un método apropiado para la interpretación del balance de S en estos suelos.

**Palabras claves:** sulfato, Andisol, turbidimetría, cromatografía iónica

## ABSTRACT

Sulphur (S) is an essential crop nutrient, and its deficiency in the soil has been reported in recent years. The index of S fertility is based on the sulphate availability measured by the turbidimetry method (TB), because it is easily and quickly applied. However, this method has shown a large variability, and lack of precision to determine sulphate, particularly in Andisols, so S fertility assessment in this type of soil is not certain. The objective of this study was to evaluate the applicability of the ion-chromatography method (IC) to obtain more accurate and precise results of the available S in volcanic soils of Chile. Two sites contrasting soil and climate conditions were

assessed in their available sulphate content by the TB and IC methods. The IC method was tested for accuracy and precision by calculating the curve of calibration and by comparing sulphate in the soil extracts ( $n=10$ ) with the addition of standard concentrations to the same extracts. Values of available S in the Andisol varied depending on the methodology used ( $P \leq 0.05$ ), whilst no differences were observed in the Inceptisol ( $P \geq 0.05$ ). The IC showed linearity ( $R^2 = 0.9998$ ) and precision, with no significant differences between the measured and modelled value of sulphate ( $P \geq 0.05$ ). A wide range of available S was found in others sites ( $7-37 \text{ mg SO}_4^{-2} \text{ kg soil}^{-1}$ ), which highlights the extend of available S in Andisols and the relevance of an appropriate methodology for the interpretation of the S balances in these soils.

**Key words:** sulphate, Andisol, turbidimetry, ion-chromatography.

## INTRODUCTION

Sulphur (S) has been acknowledged as an essential element for plant growth and production, and animal nutrition, but its importance has been disregarded for many years. The functional presence of S-groups is crucial for the activity of biomolecules involved in plant metabolism, such as coenzymes and prosthetic groups, and biotin (Hawkesford et al., 2012). Crops uptake S from the soil as sulphate anion ( $\text{SO}_4^{-2}$ ), the more oxidized form of S, which is the reference tested for soil S availability (Eriksen, 2009).

Sulphate is also the final form of most of the mineral and organic transformations within the S cycle, but the study of S turnover has not been particularly straightforward, due to the various complex biochemical transformations challenging the methodology for S measurements. Tabatabai and collaborators made a significant contribution regarding S methods (Tabatabai and Bremner, 1972; Tabatabai 1996) to validate the compartments size and the fate of S precisely, but they are difficult to implement and apply because they are time-consuming and due to the toxic compounds released during the procedure. This affects the estimation of the soluble sulphate in theoretical and practical aspects, i.e., modelling for a better understanding of the cycle and for S fertilizer recommendations, and assessing the relationship with other elements in the soil organic matter, such as nitrogen and phosphorous.

The methodology to measure the soil available S, the pool of soluble and adsorbed sulphate, implies an extraction of the sulphate anions with water or a salt solution, and then a specific measurement of the sulphate concentration in the extract. There are several methods to assess this second phase, but the turbidimetry method is widely used because the procedure is rapid and the method is easy to apply. However, the colorimetric determination has shown to be largely variable and imprecise, i.e., the repeatability shows different values, particularly for volcanic ash-derived soils with large organic matter contents. The principle of the

method is based on the extraction of sulphate using a phosphate solution because of the greater ionic affinity of this anion that replaces the sulphate anions at the colloidal adsorption sites, and its close relationship with the S pool used for crop nutrition (Tabatabai, 1996). A solution of dihydrogen calcium phosphate  $-\text{Ca}(\text{H}_2\text{PO}_4)_2$  is usually used because of the desirable calcium property to reduce dispersion of organic colloids, and after a period of shaking and filtration, a Ba-solution is added to the extract producing  $\text{BaSO}_4$  (Sadzawska and Massaro, 1993). The turbid aspect of this precipitate is later related to the sulphate concentration by absorption spectroscopy using 440 nm length waves, from a calibration model between standard concentrations of sulphate and the intensity of the colour extract. The organic-Al complex colloids in volcanic soils react with Ba forming a colour that is an artefact reaction rather than the expression of S concentration, leading to lower sulphate values. This issue has been previously addressed by Ajwa and Tabatabai (1993), who tested different extracts and sulphate analysis against the well-known method of Tabatabai (1996), and the chromatography method showed the best results, particularly for volcanic soils. They reported coefficients of variation between 4.4 to 28.5% for turbidimetry measurements, and only 2.0-7.5% for the ion chromatography method.

The ion-chromatography method was described as an alternative method for nitrate and sulphate determinations more than 30 years ago (Dick and Tabatabai, 1979), but advances in technology have made it more accessible. Briefly, an eluent stream (mobile phase) carries the soil extract towards an analytic column (stationary phase), that separates the anions contained in the soil extract by ion exchange, to flow then to the suppressor column where the eluent conductivity is suppressed. The ion is detected through a conductivity cell that measures electrical conductance and its signal is transmitted to a data collection system. The sulphate determination using this technique is straightforward, and despite of the high initial cost of the equipment (Ajwa and Tabatabai, 1993), the

benefit of an accurate soil/plant sulphur diagnosis is worthy, particularly in volcanic soils.

Volcanic soils (Andisols) represent a small area of agricultural land in the world (124 mill hectares, 0.84% of the world surface, Mc Daniel et al., 2012), but large population relies on the productivity of this type of soil. The Andisols have positive physical and chemical properties (Sandoval et al., 2007; Takahashi and Dahlgren, 2016). In Chile, agricultural systems produced under volcanic soils (43% of the agricultural land) are cereal rotations, pastures and grasslands. The levels of available S reported are overall low (Aguilera et al., 2002, Alfaro et al., 2006). Despite the disregard on soil S levels, an application of 20 to 30 kg S ha<sup>-1</sup> is generally recommended. A more precise measurement of the available sulphate is needed in order to assess the fertilization strategies, to manage the protein level in grains and grasses, the S compounds in rape crops, as well as to improve the quality of grasslands and prairies species (Zaman et al., 2014), and also to better understand the S cycle in Andisols. For example, the authors have found differences of 6 to 10 mg kg<sup>-1</sup> of available S for the same soil sample obtained by the turbidimetric method in an Andisol soil. Therefore, this study aims to assess the applicability of the ion-chromatography method to obtain more reliable measurements of the available S in volcanic soils of Chile to optimise future soil S agronomic management.

## MATERIALS AND METHODS

**Soil sampling and experiments.** A volcanic (Andisol, Andes pre-mountains, 36°59' S; 71°55' W) and an alluvial soil (Inceptisol, Depression between Andes and Coastal Range, 34°33' S; 71°22' W) were sampled in autumn. The sites differ in soil organic matter content (SOM) and annual rainfall. Rainfall is 1500 mm year<sup>-1</sup> in the Andisol and 600 mm year<sup>-1</sup> in the Inceptisol. The chemical soil properties of the Andisol were: 11% of soil organic matter (SOM), pH 6.17, 14.3 mg kg<sup>-1</sup> N-NO<sub>3</sub><sup>-</sup>, 14.6 mg kg<sup>-1</sup> P (Olsen), 324 mg kg<sup>-1</sup> K; whilst the Inceptisol showed 2.5% of SOM, pH 6.36, 15.5 mg kg<sup>-1</sup> N-NO<sub>3</sub><sup>-</sup>, 10.1 mg kg<sup>-1</sup> P (Olsen), 191 mg kg<sup>-1</sup> K.

Experiment 1. Random soil samples (n = 10) were taken from each site at 0-10 cm depth (a more active layer likely to contain more organic matter so as to measurable S supply). In order to test the quantification of available S in the Andisol soil, soil sulphate was measured by turbidimetry and ion-chromatography methods, using the same soil extracts, using the Inceptisol as a control treatment.

Experiment 2. Once the comparison of S availability between methods was proved, other

Andisol soils were sampled (0-23 cm) to test the measurements of soil sulphate on the arable depth using the ion-chromatograph technique, and determine the levels of available S under different agronomic management and climate conditions. This was not done to test the technique, but to briefly detect available S from different agrosystems based on Andisol soils; an Alfisol was also used as a control treatment. Soils from the outskirts of the Andes Mountains, the Mediterranean dryland of Central Chile, and from Western Patagonia (Del Pozo and Del Canto, 1999; Hepp 2014; Stolpe and Hepp, 2014) were tested for this purpose.

**Instrumental assessment of ion chromatography analysis.** The calibration curve method (CCM) was used by modelling a function that fit the standard concentrations of sulphate and their signal intensity. The standard solutions were 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 13, 16, 19, 22, 25, 28, 31, 40 and 50 mg L<sup>-1</sup> of SO<sub>4</sub><sup>-2</sup>, according to the expected concentrations in the samples, prepared in Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> solution. Furthermore, the standard addition method was also applied by using increasing volumes of a standard sulphate solution added to a number of soil extracts (n = 10), 2 mL, 4 mL, 10 mL (in triplicates), then measuring the total concentration of sulphate. The exact amount in the soil is the difference between the measured sulphate and the added volume. The standard deviation was used to compare the precision of these measurements.

The limit of detection of sulphate (LD) was estimated as LD = 3.3 σ m<sup>-1</sup>, where σ is the standard deviation of the signal from the blank solution (n = 15), and m is the slope of the CCM.

**Soil treatment and sulphurextraction.** This first step was common for all the samples and then aliquots from each soil extracts were used to measure the sulphate concentration by turbidimetry and ion-chromatography. Three replicates from each soil sample collected in the field were separated and air dried for 48 h at 25°C and sieved at 2 mm. The soil extraction was done over a 20 g of soil per sample, using 100 mL of Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> [0.01M], and activated carbon (0.5 g) was also added, and then shaken for 30 min and left to settle for 30 min. The extracts were centrifuged at 6000 rpm for 30 sec and filtered through Whatman 42. A second filtration was done for ion-chromatography analysis using a filter membrane of 0.45 μm.

**Available sulphur measurement.** The turbidimetry analysis was applied according to the standard procedure of laboratory analysis in Chile (Sadzawska et al., 2006). The absorbance of the extracts was measured at 440 nm, whilst 1 mL-extract samples were introduced in the

ion-chromatograph to obtain the sulphur concentration according to the retention time (min), shown as a peak reached by the sulphate ion in the chromatogram.

The records from the spectrophotometer and the chromatograph were related to a calibrated regression model to obtain the sulphate concentration. For the operative conditions of the ion chromatography (IC Dionex B 2100) an IonPac™ AS16A separation column fitted to an Ion Pac AG9A guard column were used and the eluent consisted of 25 mM KOH at a flow rate of 1 mL min<sup>-1</sup>. The retention time to quantify the sulphate signal was 5.6 min, as shown. The IC equipment was linked to the software Chromeleon 7.1 SR2 (Thermo Scientific, 2012).

**Statistical analyses.** The effect of methods and soil type were assessed applying the t-student test to compare the significance ( $P \leq 0.05$ ) of the differences between the mean values of method, soil type, and the interaction between these. To assess the precision of the ion-chromatography technique, the linearity was calculated as a regression model (Kościelniak and Wieczorek, 2016), and the F test ( $P \leq 0.01$ ) was used to evaluate the significance of the linearity.

## RESULTS AND DISCUSSION

### Assessment of the ion-chromatography method

The soil available sulphate was high in both soils (over 20 mg SO<sub>4</sub><sup>-2</sup>-S kg soil<sup>-1</sup>), regardless of the methodology used (Table 1), and the Andisol showed to have larger SO<sub>4</sub><sup>-2</sup>-S than the Inceptisol ( $P \leq 0.05$ ). The soil pH was over 6 in both types

of soils, which might have contributed to the high level of S.

Previous studies showed low level of sulphur in Andisols, i.e.,  $\leq 12$  mg SO<sub>4</sub><sup>-2</sup>-S kg soil<sup>-1</sup>, measured by turbidimetry (Aguilera et al., 2002; Alfaro et al., 2006) and  $< 1$  mg SO<sub>4</sub><sup>-2</sup>-S kg soil<sup>-1</sup>, measured by ion-chromatography (Ajwa and Tabatabai, 1993), but the range measured in this study was higher, perhaps associated to the larger content of soil organic matter in the Andisol, and the complete fertilization management applied in this field. In turn, the reported values of available S for non-volcanic soils in the Central Region of Chile vary from less than 1 mg S-SO<sub>4</sub><sup>-2</sup> kg soil<sup>-1</sup> measured by turbidimetry (Opazo et al., 2000) up to 53-131 mg SO<sub>4</sub><sup>-2</sup>-S kg soil<sup>-1</sup> (Ajwa and Tabatabai, 1993) measured by ion chromatography.

The results showed specificity in the methodology to measure the available sulphate in the Andisol, as the sulphate values in this soil obtained by TB and IC were significantly different ( $P \leq 0.05$ ), resulting in higher values when IC was used (Table 1). A larger variation of TB (CV = 23%) resulted contrasting with the low variation of IC (CV = 7%) observed in the sulphate analysis of volcanic soil.

The trend was not repeated in the Inceptisol as both types of methods showed the same level of sulphate (23 g SO<sub>4</sub><sup>-2</sup>-S g soil<sup>-1</sup>). The variability of soil sulphate was higher compared to the values measured in the Andisol since the standard deviations were around 30% and 70% higher in the Inceptisol using TB and IC, respectively. Consequently, the coefficients of variation were around 50% regardless of the applied methodology (Table 1). As the TB is already in

**Table 1. Differences in the soil available sulphate (t-Student test,  $P \leq 0.05$ ) measured by turbidimetry (TB) and an alternative methodology of ion-chromatography (IC) in two types of soils.**

**Tabla 1. Diferencias en el sulfato disponible (t-Student test,  $P \leq 0,05$ ) medido por el método rutinario de turbidimetría (TB) y el método alternativo de cromatografía iónica (IC), en dos tipos de suelos.**

		SO <sub>4</sub> <sup>-2</sup> -S (mg kg <sup>-1</sup> )		Sd <sup>2</sup> <sub>pooled</sub>	SED	t <sub>(sample)</sub>
		TB	IC			
Andisol	Media	38.66	49.05	45.01	3.00	3.46*
	Sd	8.81	3.53			
Inceptisol	Media	23.81	23.57	141.88	5.33	-0.05
	Sd	12.46	11.34			
	Sd <sup>2</sup> <sub>pooled</sub>	116.35	70.55			
	SED	4.82	3.76			
	t <sub>(sample)</sub>	3.08*	6.78*			

Sd: standard deviation; Sd<sup>2</sup><sub>pooled</sub>: pool estimated variance; SED: standard error of the difference; \* Statistical difference  $t_{(18, 0.025)} = 2.101$

use as the certified method to measure available S, the alternative methodology of IC was tested with emphasis in the Andisol, as the results showed to be sensitive to the applied method. The linearity of the IC showed a determination coefficient of  $R^2 = 0.9998$ , and the F value of the ANOVA procedure was significant ( $P < 0.001$ ), which is appropriate to guarantee the accuracy of the IC method (Kościelniak and Wieczorek, 2016), because the signal intensities measured were widely tested up to  $50 \text{ mg L}^{-1}$ . The slope of the linear regression ( $m$ ) was 0.9712, whilst the interception coefficient was 0.7804 units, and they were used to obtain the limit of detection and a test of comparison between the actual measured value of sulphate in soil extracts ( $n = 10$ ) and the modelled values from the regression of the standard addition curve, using 2, 4, and  $10 \text{ mg S-SO}_4^{-2} \text{ L}^{-1}$ , respectively, as previously described.

The limit of detection was  $0.51 \text{ mg SO}_4^{-2}\text{-S L}^{-1}$ , calculated from the extracting solution that showed a media value of  $0.291 \text{ mg SO}_4^{-2}\text{-S L}^{-1} \pm 0.153 \text{ mg SO}_4^{-2}\text{-S L}^{-1}$ , from a range of 0.044 to  $0.485 \text{ SO}_4^{-2}\text{-S L}^{-1}$ . Thus, the limit of quantification estimated as the double of the limit of detection, was  $1.02 \text{ mg SO}_4^{-2}\text{-S L}^{-1}$ , which is comparable with the  $1.5 \text{ mg L}^{-1}$  reported for one of the most advance technique, the Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) for sulphate determination (Sadzawska and Massaro, 1993). However, the equipment for this type of method is more expensive than IC. As the limit of quantification was around  $1\text{-mg L}^{-1}$ , the test for the recovery of sulphate was run starting with standard solutions of  $2 \text{ mg S-SO}_4^{-2} \text{ L}^{-1}$ .

The analysis of accuracy for the sulphate determination showed that there was no significant difference ( $P \leq 0.05$ ) between the modelled and measured values (Table 2), and so the values determined by IC would be reliable to account for sulphate in Andisol and Inceptisol soils. The difference between these values and the ones in Table 1 arises because the determination of sulphate was done in soil extractions produced

in two different occasions.

The recovery of sulphate based on the addition of the standard solutions allowed the recovery of around 95% of the added sulphate, showing however an overestimation at the smallest amount of sulphate added,  $2 \text{ mg L}^{-1}$  (Table 3). This might occur because values over  $50 \text{ mg kg}^{-1}$  were not expected under the conditions of this experiment and so the calibration was set up to this limit. Alternatively, the range measured was too close to the limit of detection, which seems to be a more sensible rationale since the percentage of recovery was well acceptable for the 4 and  $10 \text{ mg L}^{-1}$ .

#### Available sulphate tested in other soils

The IC method was used to measure available S in other volcanic soils and a non-volcanic soil (Table 4) in order to validate that the large values found in this study site were not an artefact of the determination itself. The available S in the three different Andisols was lower than the sulphate measured in the soil from "El Carmen" tested for IC method (Table 1). The range measured was between 7 and  $37 \text{ mg SO}_4^{-2}\text{-S kg soil}^{-1}$ , showing the plasticity of the IC method to quantify in a wide range of sulphate concentrations in Andisols, which is extended to less than 1 up to  $37 \text{ mg SO}_4^{-2}\text{-S kg soil}^{-1}$  when the non-volcanic soil is also included. As the range of availability is classified as very low ( $< 6 \text{ mg S-SO}_4^{-2} \text{ kg soil}^{-1}$ ), low ( $6\text{-}12 \text{ mg S-SO}_4^{-2} \text{ kg soil}^{-1}$ ), medium ( $12\text{-}20 \text{ mg S-SO}_4^{-2} \text{ kg soil}^{-1}$ ), high ( $20\text{-}30 \text{ mg S-SO}_4^{-2} \text{ kg soil}^{-1}$ ), and very high ( $> 30 \text{ mg S-SO}_4^{-2} \text{ kg soil}^{-1}$ ), the values measured by IC from different soils encompass all categories of availability. These values represent the available balance for crop nutrition, and it seems that the particular agronomic management would affect the S transformation in Andisols, i.e., Andisols in South-central Chile compared with the Andisols in Western Patagonia Region.. Furthermore, there are also differences within the same area of volcanic soils sampled in this study (the outskirts of the Andes mountains), where

**Table 2. Comparison between values of sulphate obtained from a regression model and actual measurements by ion-chromatography in an Andisol and Inceptisol, respectively.**

**Tabla 2. Comparación entre los valores de sulfato obtenidos de un modelo de regresión y de las mediciones por cromatografía iónica en un Andisol y un Inceptisol, respectivamente.**

	Andisol*	Inceptisol
$\text{SO}_4^{-2}\text{-S (mg kg}^{-1}\text{) measured in soil extracts}$	50.48 (4.97)**	18.71 (13.31)
$\text{SO}_4^{-2}\text{-S (mg kg}^{-1}\text{) modelled}$	52.66 (4.93)	17.58 (12.88)
LSD (Fisher, $P < 0.05$ )	2.51	7.48

\* "El Carmen" site

\*\*Values between brackets are the standard deviation of the sample ( $n = 10$ )

**Table 3. Recovery of the standard sulphate solutions added to soil extracts of an Andisol.****Tabla 3. Recuperación de las soluciones estándar de sulfato adicionadas a los extractos de suelo de un Andisol.**

	Mean SO <sub>4</sub> <sup>-2</sup> -S (mg kg soil <sup>-1</sup> )	Recovery (%)
SO <sub>4</sub> <sup>-2</sup> -S added (mg kg soil <sup>-1</sup> )		
0	50.48 (4.56)*	
2	52.86 (4.71)	118
4	54.28 (4.93)	95
10	60.12 (5.40)	96

\*Values between brackets are the standard deviation of the sample (n = 10)

**Table 4. Available sulphur in volcanic and non-volcanic soils in some regions of Chile measured by ion-chromatography.****Tabla 4. Azufre disponible en suelos volcánicos y no-volcánico en algunas regiones de Chile, medido por cromatografía iónica.**

	Yungay	Yungay-2	Santa Elena	Cauquenes
Soil order	Andisol	Andisol	Andisol	Alfisol
Agricultural productive area	Andes pre-mountains South-central Region		Simpson Valley Intermediate zone of Western Patagonia Region	Mediterranean dryland South-central Region
Location	37°8.76' S; 71°56.4' W	37°8.78' S; 71°57.08' W	45°45' S; 72°03' W	35°57.42' S; 71°17.42' W S;
Rainfall (mm)	1400	1400	1000	695
Land use	Cereals crop rotation Oat-wheat (no-till)	Oat-wheat	Grassland	Degraded grassland
Available S (mg kg <sup>-1</sup> )	37.46 (0.25)*	15.12 (0.27)	7.16 (0.16)	0.06 (0.01)

\*Values between brackets are the standard deviation of the sample (n = 3).

values of available S were 15 (Yungay 2 site), 37 (Yungay site), and around 50 mg SO<sub>4</sub><sup>-2</sup>-S kg soil<sup>-1</sup> (El Carmen site).

### CONCLUSION

The availability of S extracted using a dihydrogen calcium phosphate solution showed different values depending on the method of determination in Andisols. The values of SO<sub>4</sub><sup>-2</sup>-S obtained from the IC method were larger than those from the TB determination. This difference reached an average value of 10 mg sulphate kg soil<sup>-1</sup>, but the IC determination proved to be an accurate method to measure sulphate (P < 0.05).

There was no artefact in the reported values and IC method produced reliable results when applied in volcanic soils from different sites and agronomic management. Therefore, the IC is recommended to measure sulphate and to assess the status of S fertility in Andisols.

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